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(54) Title: FOAMED POLYESTERS FOR IRRADIATED STERILIZATION PACKAGING

(57) Abstract: The invention provides packages comprising articles sterilized by irradiation and packaged within foamed polyester packaging. The invention also provides methods for the sterilization, by irradiation, of articles contained within foamed polyester packaging. The sterilized articles include food products, medical instruments, and other articles which are typically sterilized before consumption or use. The packaging may comprise a mono-layer or multi-layer structure. The irradiation can be created by various radiation sources such as an electron beam source or a radioactive source. The foamed polyester is made from repeat units of a diacid component having at least 65 mole percent terephthalic acid, naphthalenedicarboxylic acid, 1,3-cyclohexanedicarboxylic acid, 1,4-cyclohexanedicarboxylic acid, or mixtures thereof, and repeat units of a glycol component having at least 65 mole percent ethylene glycol, neopentyl glycol, 1,3-cyclohexanemethanol, 1,4-cyclohexanemethanol, or mixtures thereof.

FOAMED POLYESTERS FOR IRRADIATED STERILIZATION PACKAGING

TECHNICAL FIELD OF THE INVENTION

The invention relates to materials and methods used for the packaging of articles. More particularly, the invention relates to materials and methods used for packaging of articles which are sterilized by irradiation.

BACKGROUND OF THE INVENTION

Plastic materials are widely used in the packaging industry because of plastic's ability to protect a product from physical damage, loss, and other degradation. In addition, plastic material facilitates the handling of the resultant product—from the time of packaging to the time of distribution to the consumer. However, in view of recent food product contamination from harmful bacteria such as Salmonella or E. coli, considerable interest has arisen in processes and materials for improved packaging to better enable sterilization.

An attractive process that has emerged involves the sterilization of a packaged food by irradiation. Although the irradiation process has better enabled sterilization, the process has unfortunately limited the number of plastics that can be used for packaging.

For example, flexible packages made from films or thin sheets of polyolefins or plasticized poly(vinyl chloride) have been irradiated. However, the irradiation has adversely affected the properties of the packaging material. The polyolefins are readily cross-linked by irradiation techniques, and plasticized poly(vinyl chloride) can become discolored. As another example, recent issues about levels of styrene monomer in polystyrene and in polystyrene foam have raised concerns about using polystyrene packaging for irradiation sterilization.

Polyesters have been irradiated with radiation capable of sterilization. However, such radiation has been confined to polyester films, sheets, and other solid polyesters. Unfortunately solid polyesters are inherently heavy and less flexible than a comparable lightweight material. Lightweight polyesters—such as a polyester foam—which are substantially less costly and easier to handle during

storage and shipping than their solid counterparts, have not been found in the prior art as packaging for irradiated products.

Processes and materials of the prior art are described by the following references:

Encyclopedia of Chemical Technology, "Food Packaging", Volume 11, 4th Edition, 1994, pp. 834-856, John Wiley and Sons, describes various aspects of food packaging, including packaging materials, foods, and requirements for packaging. The reference does not describe foamed polyester.

Judy Rice, Packaging Network: Virtual Community for the Packaging Network, "Electron-Beam Irradiation of Packaged Foods", November 12, 1999, describes certain aspects of irradiation of packaged foods for non-polyester materials.

S. E. Harvey, Imperial Chemical Industries Wilton Materials Research Centre, "Packaging for Irradiated Food", Presented at Irradiation Symposium, March 1-2, 1990, London, England, describes the irradiation of packaged foods. Such foods include spices, shellfish, and dried fruit. Plastic materials including poly(ethylene terephthalate) are described, but not foamed polyester.

N. G. S. Gopal, Packaging India, "Effects of Radiation Sterilization on Packaging Materials", October-December, 1975, pp. 9-15, describes the effects of radiation sterilization on packaging materials, including polystyrene, polyethylene (low, medium, high density), certain nylons, certain polyolefins, polyvinyl chloride, certain polyesters, polycarbonate, and other materials. The reference does not describe foamed polyester.

Anonymous, "Packaging Materials for Use in Radiation", Food Engineering, Vol. 61, 73-74 (1989), describes the irradiation of various packaging materials, including poly(ethylene terephthalate). The reference does not describe foamed polyester.

J. J. Killoran, Radiation Research Reviews, "Chemical and Physical Changes in Food Packaging Materials Exposed to Ionizing Radiation", Vol. 3, 369-388 (1972), describes the electron beam and gamma irradiation of various

packaging materials, including poly(ethylene terephthalate). The reference does not describe foamed polyester.

K. A. Riganakos et al, "Effects of Ionizing Radiation on Properties of Monolayer and Multilayer Flexible Food Packaging Materials", Radiation Physical Chemistry Journal, Vol. 54, 527-540 (1999), describes the irradiation of various food packaging materials, including poly(ethylene terephthalate). The reference does not describe foamed polyester.

Noemi Chuaqui-Offermans, "Packaging Materials for Use in Irradiation", Food Engineering, April 1989, pp. 73-74, describes the irradiation of various food packaging materials. The reference does not describe foamed polyester.

I. Steiner et al, "About the Influence of Various Sterilization Methods on the Chemical and Physical Properties of Food Packaging Materials", Plastics, Lebensmittelchemie, Vol. 53, 53-64 (1999), describes the sterilization of various food packaging materials. The reference does not describe foamed polyester.

N. I. Zhitariuk et al, "Tensile Properties of Electron Irradiated Track Membranes", European Polymer Journal, Vol. 32, 391-395 (1996), describes the affect of irradiation on the tensile properties of certain plastics including poly(ethylene terephthalate). The reference does not describe foamed polyester.

David Kilkast, "Prospects for Food Irradiation", Chemistry and Industry, March 5, 1990, pp. 128-130, describes the irradiation of unpackaged food.

D. W. Allen et al, "Gamma-Irradiation of Food Contact Plastics: The Rapid Destruction of an Arylphosphite Antioxidant in Polypropylene", Chemistry and Industry (1987), describes the irradiation of polypropylene.

D. W. Allen et al, "Effects of Gamma-Irradiation on Hindered Phenol Antioxidants in PVC and Polyolefins", Chemistry and Industry (1986), describes the irradiation of poly(vinyl chloride) and polyolefins.

R. M. Morrison, "Food Irradiation Still Faces Hurdles", Food Review, Vol. 15, 11 (1992), describes the irradiation of unpackaged food.

Judy Rice, "Irradiating Prepackaged Poultry", Food Processing , Vol.55, 44 (1994), describes the irradiation of food packaging including polystyrene foam

and certain non-foamed polymers. The reference does not describe foamed polyester.

Maureen Byrne, Food Engineering International, Vol. 21, 37 (1996) "Irradiation Update", describes the irradiation of unpackaged food.

F. Bourges et al, "Effects of Electron Beam Irradiation on Commercial Polypropylene", Packaging Technology and Science, Vol. 5, 197-204 and 197-204 (1992), describes the irradiation of polypropylene as a food packaging material.

F. Bourges et al, "Effects of Electron Beam Irradiation on Commercial Polyolefins", Packaging Technology and Science, Vol. 5, 197-204 and 205-209 (1992), describes the irradiation of polyolefins as food packaging materials.

R. Buchalla et al, "Effects of Ionizing Radiation on Polymers. A Compilation of Literature Data", Part 1-Food Packaging Materials, Institute for Social Medicine and Epidemiology of the German Health Office (published in Berlin in 1992, 222 pages), describes the irradiation of food packaging polymers. The reference does not describe foamed polyester.

Lee Mooha et al, "Irradiation and Packaging of Fresh Meat and Poultry", Journal of Food Protection, Vol 59, 62-72 (1996), describes the irradiation of food packaging polymers. The reference does not describe foamed polyester.

L. Katan, "Irradiation of Food Packaging", Paper Presented at Conference on Food Packaging at London, England, March 4-5, 1992, generally describes public acceptance and economics of the irradiation of food packaging.

J. H. O'Donnell, "Chemistry of Radiation Degradation of Polymers", ACS Symposium Series No. 475, edited by R. L. Clough and S. W. Shalaby, presented at the 200th National Meeting of the ACS at Washington, DC, August 26-31, 1990, describes the irradiation of polymers such as poly(vinyl chloride), polystyrene, and an ethylene-propylene copolymer. The reference does not describe foamed polyester.

R. T. Toledo, "Overview of Sterilization Methods for Aseptic Packaging Materials", ACS Symposium Series 365, edited by J. H. Hotchkiss, presented at

193rd Meeting of the ACS at Denver, Colorado, April 5-10, 1987, describes the irradiation of polymers such as polyethylene, ethylene co-polymers, polystyrene, poly(vinylidene chloride), and polyacetals. The reference does not describe foamed polyester.

European Patent Application EP 0 542 464 A1 describes blends of polycarbonate containing 5 to 18 weight % of an unmodified poly(1,4-cyclohexylenedimethylene terephthalate) polyester. These blends are reported to have less yellowing tendency when irradiated with gamma irradiation for medical packaging. The reference does not describe foamed polyester.

Tamehiko Ikeda, European Patent Application EP 0 895 719 A1 describes the infrared cooking and sterilization of foods in a plastic container which may be made from a wide range of plastic materials including poly(ethylene terephthalate). The patent does not describe foamed polyester.

U.S. Patent 4,480,086 describes copolyester compositions based on 65-100 mole % 1,4- cyclohexanedicarboxylic acid, 65-100 mole % of 1,4-butanediol and 15-35 mole % of dimer acid or dimer glycol which are reported to be resistant to gamma radiation. The patent does not describe foamed polyester.

WIPO Patent Application WO 98/16287 A1 describes a method of sterilizing poly(ethylene terephthalate) bottle materials. The patent application does not describe foamed polyester.

U.S. Patent 5,366,746 describes a high temperature pasteurization and electron beam technology for sterilization of meat products. The patent describes the electron beam irradiation of meat in a polyethylene or polypropylene package. The reference does not describe foamed polyester.

In view of the state of the prior art, as described by the above references, what is needed is a lightweight material—such as a polyester foam—which can be used without substantial degradation for irradiated sterilization of packaging systems.

BRIEF SUMMARY OF THE INVENTION

The invention relates to a package containing an article sterilized by irradiation. The article is enclosed in a space defined by surrounding packaging which comprises foamed polyester. The package comprises a sterilized environment formed by irradiating the space.

The article includes food products, medical instruments, and other articles which are typically sterilized before consumption or use. The packaging may comprise a mono-layer or multi-layer structure. The irradiation can be created by various radiation sources such as an electron beam or a radioactive source, and is capable of sterilizing the articles.

The invention also relates to a method comprising the step of sterilizing, by irradiation, an article contained within packaging comprising foamed polyester.

The invention further relates to a method for making a sterilized packaged article comprising the step of irradiating the article within packaging comprising foamed polyester.

The invention still further relates to sterilized packaged articles made by methods of the invention.

DETAILED DESCRIPTION OF THE INVENTION

The invention relates to the novel and unexpected use of foamed polyester polymers as packaging materials for articles which are sterilized by irradiation. The foamed polyesters are unexpectedly shown to have substantially no degradation in physical properties after being irradiated with irradiation sufficient to create sterilized conditions.

One aspect of the invention relates to foamed polyesters which are used for the packaging of irradiated articles.

Another aspect of the invention relates to packages comprising irradiated articles packaged within foamed polyester packaging.

Still another aspect of the invention relates to methods for irradiating articles which are packaged within foamed polyester packaging.

A further aspect of the invention relates to methods for making sterilized packaged articles comprising the irradiation of such articles in packaging comprising foamed polyester.

A still further aspect of the invention relates to sterilized packaged articles made by various methods of the invention.

These aspects and other aspects of the invention are described herein.

Articles within the scope of the invention include food products, medical instruments, and other articles which can be sterilized before consumption or use.

Polyesters suitable for the invention comprise repeat units of a diacid component having at least about 65 mole percent, preferably at least about 80 mole percent, terephthalic acid, naphthalenedicarboxylic acid, 1,3-cyclohexanedicarboxylic acid, 1,4- cyclohexanedicarboxylic acid, or mixtures thereof. Although any naphthalenedicarboxylic acid isomer, or mixture thereof, is suitable, the 1,4-, 1,5-, 2,6- and 2,7- isomers are preferred. In addition, the 1,4-cyclohexanedicarboxylic acid particularly may be the cis isomer, trans isomer, or mixtures thereof. The diacid component is based on 100 mole percent.

The polyesters may also comprise up to about 35 mole percent, preferably up to about 20 mole percent, modifying diacids. Suitable modifying diacids include those containing about 4 to about 40 carbon atoms. Typical examples include, but are not limited to, succinic, glutaric, adipic, sebacic, suberic, dimer, isophthalic, sulfoisophthalic, and other similar diacids, including derivatives, such as various esters, or anhydrides.

Polyesters suitable for the invention also comprise repeat units of a glycol component having at least about 65 mole percent, preferably at least about 80 mole percent, ethylene glycol, neopentyl glycol, 1,3-cyclohexanedimethanol, 1,4-cyclohexanedimethanol, or mixtures thereof. The 1,3- and 1,4-cyclohexanedimethanol may be the cis isomer, trans isomer, or mixtures thereof. The glycol component is based on 100 mole percent.

The polyesters may also comprise up to about 35 mole percent, preferably up to about 20 mole percent, modifying glycols. Suitable modifying glycols include those containing about 3 to about 12 carbon atoms. Typical examples include, but are not limited to, propylene glycol, 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,8-octanediol, 2,2,4,4-tetramethyl-1,3-cyclobutanediol, and other similar glycols.

Although virtually any homopolymer or copolymer with the components described above could be used, specific examples—though non-limiting—include: poly(ethylene terephthalate) (PET), poly(ethylene naphthalenedicarboxylate) (PEN), poly(1,4-cyclohexylenedimethylene terephthalate) (PCT), and poly(1,4-cyclohexylenedimethylene naphthalenedicarboxylate) (PCN). Typically the polymers can be produced using melt phase and/or solid phase polycondensation techniques well known in the art.

The polyesters of the present invention can be readily foamed by the techniques described in U.S. Patent Nos. 5,399,595, 5,482,977, 5,519,066, 5,696,176, and 5,654,347. A preferred foaming process is described in 5,654,347. All the above patents are incorporated herein by reference.

Suitable foamed polymers will have inherent viscosity (I.V.) values in the range of about 0.4 to about 1.5 dL/g; those having I.V. values of 0.8 to 1.5 dL/g are preferred because of superior foaming characteristics. When using polyesters with a lower I.V., it is desirable to include an agent such as one or more chain extending agents or one or more branching agents to increase the melt strength of the polyester to improve its foaming characteristics. Such chain extending agents include polyfunctional monomers containing at least 2 or more functional reactive groups, and such branching agents include polyfunctional monomers containing at least 3 or more functional groups. Suitable chain extending agents include, but are not limited to, various bifunctional monomers including, for example, diols, diacids, diamines, and other similar monomers. Suitable branching agents include, but are not limited to, polyfunctional acids,

polyols, and hydroxy acids containing about three to about six functional groups. Typical branching monomers include, but are not limited to, trimesic acid, pyromellitic acid, pyromellitic dianhydride, trimellitic anhydride, citric acid, malic acid, tartaric acid, trihydroxyglutaric acid, 3-hydroxyglutaric acid, trimethylolpropane, pentaerythritol, glycerol, sorbitol, and the like. Other suitable branching agents are disclosed in U.S. Patent No. 5,654,347. The chain branching and chain extending monomers are generally used in concentrations ranging from about 0.01 to about 2.0 mole percent. They may be employed in the fabrication of the polymer using techniques well known in the art. In particular, they may be included with the starting monomers used to make the polyester, or they may be added to a preformed polyester. A preferred method involves using a master batch of a branching agent in a polyolefin which is melt mixed with a preformed polyester as described in U.S. Patent No. 5,654,347.

The foamed polyesters of the present invention will generally have densities of about 0.1g/cc to about 1.0 g/cc; densities of about 0.2 g/cc to about 0.9 g/cc are preferred. The foamed polyesters are typically in sheet form having a thickness of about 5 mils (0.125 mm) to 90 mils (2.25 mm), preferably about 10 mils (0.25 mm) to about 40 mils (1 mm).

Suitable blowing agents for the foaming process include a variety of chemical and physical blowing agents, or combinations thereof. The foamed polyester sheet should be produced in such a manner as to have about 2% to about 40% crystallinity, preferably about 5% to about 20% crystallinity, and more preferably about 5% to about 10% crystallinity. The sheeting optionally may contain crystallization nucleating agents, gas cell nucleating agents, pigments to impart color, impact modifiers, or other modifying components known to those skilled in the art.

The sheeting may be a mono-layered or a multi-layered structure. Although a multilayer structure comprises at least one layer of foamed polyester, the structure may also comprise one or more layers of non-foamed polyester materials. In addition, a multi-layer structure may comprise one or more layers of

non-polyester materials or mixtures of polyester and non-polyester materials. The multi-layered structures may be prepared through co-extrusion processes or lamination processes. Such sheeting is readily vacuum drawn to provide suitable containers for the storage of various products. Various forming techniques may be used for forming a container. Single or two staged processes may be used to form a container having between about 2% and about 40% crystallinity. The containers may or may not be thermally or oven stable. Matched metal tooling may also be used to mold the container. The tooling may be heated or cooled to achieve the desired level of crystallinity. The specific technique for forming the container is not critical. Other forming techniques would be obvious to those skilled in the art.

After foaming the container, an article such as a food product or one or more medical instruments may be placed in the container. After placing the article in the container, the container may be closed with a closure lid. In the resultant package, the article typically resides in the environment of a space surrounded by the container and the closure lid. Typical closure lids include, but are not limited to, a clear lidding film, a hermetically sealed film or bubble cap, and a lidding made from polyester foam. The clear lidding film allows the product to be viewed and is preferably a film having a thickness of about 0.5 mils (0.0125 mm) to about 20 mils (0.5 mm). Such a film is typically made of one or more polymers that have high gas barrier properties such as PET or PEN. The film may be monolayer or multilayer. Depending on the article and the storage conditions, the atmosphere in the space may be air, nitrogen, oxygen, carbon dioxide, carbon monoxide, ethanol, sulfur dioxide, argon, other similar gases, or mixtures thereof to provide a controlled atmosphere or modified atmosphere in the space. The precise nature of the closure lid or the atmosphere is not critical to the invention. Accordingly other closure lids or atmospheres could be used without deviating from the invention. If the article is a food product such as fresh meat, poultry, or other similar food, it may be desirable to place the product in the

container on a porous paper or nonwoven fabric to absorb liquids which may flow from the product.

Radiation sources useful for the invention include various sources of high energy radiation capable of sterilizing articles such as food products or medical instruments. Such radiation includes electron beam radiation, radiation from radioactive sources (such as gamma ray radiation, radiation from alpha particles, or radiation from beta particles), x-rays, and other similar forms of radiation. Typical specific sources include, but are not limited to, an electron beam source and a cobalt 60 gamma ray source. The amount of radiation required will be dependent on the article and its intended end use. Typically, radiation of about 1 to about 10 kilo-grays (kGy) is suitable, and from about 4 to about 7 kGy is preferred.

Irradiation treatment can degrade physical properties (such as mechanical, thermal, and color properties) of non-foamed plastic materials. Irradiation treatment is especially harmful to poly(vinyl chloride) products which contain plasticizers and polyolefins having phenolic stabilizers, for the treatment can readily destroy the plastic. Although non-foamed polyester materials are relatively unaffected compared to other plastic materials, one could expect that irradiation would substantially degrade the physical properties of foamed polyesters because of their inherently thin cell walls. The foamed polyesters of the present invention have been unexpectedly found to incur irradiation treatment with substantially no loss of physical properties. Accordingly, such foamed polyesters have been unexpectedly found to be able to be irradiated for sterilization purposes.

More specifically, foamed polyester containers can be readily penetrated by various radiation sources and their physical properties will not be affected. Such physical properties include the mechanical properties, thermal properties, and color properties described in Table I. As additional benefits, the foamed containers are light in weight, readily formed, cost effective, easy to stack and ship, and more economically attractive when compared to their solid

counterparts. Furthermore, food products packaged in foamed crystalline polyester containers may be easily heated within a microwave oven immediately prior to consumption.

As another benefit, copending U.S. application 09/258849, filed February 26, 1999 and incorporated herein by reference, discloses foamed polyesters similar to those of the present invention. In U.S. application 09/258849, the polyesters are shown to have unexpectedly good gas barrier properties after foaming. In view of the foamed polyesters of the present invention having essentially no loss of physical properties after irradiation, the foamed polyesters of the present invention are also expected to retain good barrier properties after irradiation.

Articles such as food products and medical instruments may be sterilized after being packaged in the foam containers. The invention may also be used for the sterilization of containers in other processes such as an aseptic food packaging process. Typical food products which may be sterilized in the containers include, but are not limited to, meats, fish, poultry, cheeses, fruits, vegetables, nuts and the like. In addition, the invention may be used for all types of foods including cooked, chilled, prepared, and raw foods. Typical medical instruments which may be sterilized include, but are not limited to forceps, scalpels, clamps, catheters, stents, grafts, injection needles, and other devices used for medical activity. However, the particular article is not critical. For example, virtually any food product, medical instrument, or other article, which can be sterilized by radiation, may be packaged in the containers of the invention.

Similarly, once the article is sterilized, the shelf life of the article is not critical to the invention. In many cases, the packages will be stored for use for only about 1 to about 10 days. However, in some cases, storage may be for up to about 1 year, or longer.

The packaging materials of this invention are primarily based on commercially available polyesters which are economical to use and are

recyclable. Typically, they do not contain chlorine and do not require the use of expensive high barrier laminated materials. However, no material is excluded from the foamed polyesters of the invention if the material satisfies the requirements described herein.

Inherent viscosity (I.V.) as used herein refers to viscosity determinations made at 25°C using 0.50 gram of polymer per 100 mL of a solvent composed of 60 weight percent phenol and 40 weight percent tetrachloroethane. The basic method of determining the I.V. of a polyester is set forth in ASTM method D2857-95.

This invention can be further illustrated by the following examples of preferred embodiments thereof. Two comparative examples directed at non-foamed polyesters are also provided. The examples are included merely for purposes of illustration, and are not intended to limit the scope of the invention unless otherwise specifically indicated.

EXAMPLES

Example 1: PET Foamed Tray

Packaging trays were made by thermoforming an approximately 0.025 inch (0.625 mm) thick, 3-layer foamed PET polyester sheet into the desired shape. The top and bottom layers were solid PET materials and the center layer was foamed PET. The top and bottom layers comprised about 10% each of the total thickness. The sheet was extruded on a 4.5 inch (112.5 mm) single barrel extruder equipped with 2 smaller satellite extruders and a flat sheet extrusion die. The foamed layer consisted of 97.8% by weight of an 0.80 I.V. homopolymer PET resin, 2% by weight Eastman Chemical Company additive G4ZZZ-3AZZ, which is commercially available, and 0.2% by weight of an endothermic chemical blowing agent Hydrocerol HK40B, manufactured by Boehringer Ingelheim of Ingelheim, Germany. A physical blowing agent (nitrogen) was injected into the extruder via a gas injection system. The melt temperature was approximately 525°F (274°C). The sheet forming temperature was approximately 350°F

(176.5°C). The approximate size of the thermoformed trays was 6 inches (150 mm) x 8 inches (200 mm). The overall density of the trays was about 0.60 g/cc. The trays were subjected to a 7.6 kGy gamma ray radiation source to simulate the radiation sterilization process. The trays were then subjected to physical and analytical analyses and compared to a control, non-radiated foamed tray. The radiated samples and the controls were tested for inherent viscosity, molecular weight distribution by gel permeation chromatography, thermal characteristics by differential scanning calorimetry, ASTM D2244 Color Analysis, and ASTM D882 Tensile properties. The results are found in Table I. There were no significant differences in any of the test results when compared to results from non-radiated control samples.

<u>Example 2: PET Foamed Trays</u>

Packaging Trays were prepared as in Example 1. The trays were then subjected to an electron beam radiation source with a dosage of 7 kGy. The trays were then subjected to analytical and physical testing as described in Example 1 and compared to a control, non-radiated sample. The test results are also found in Table I. There were no significant differences in any of the test results when compared to results from non-radiated control samples.

Example 3: Foamed PET Tray

Packaging trays were formed from approximately 0.040 inch (1.0 mm) thick mono-layered foamed sheet manufactured from PET materials as described in Example 10 of U.S. Patent No. 5,654,347. The trays were formed into a matched metal mold to allow for post extrusion expansion. The final thickness of the trays was about 0.075 inch (1.88 mm). The approximate size of the trays was 10.5 inches (262.5 mm) x 6 inches (150 mm). The density of the trays was about 0.25 g/cc. The trays were subjected to a 7.6 kGy gamma radiation source to simulate the radiation sterilization process. The trays were tested as in Example 1. The results are found in Table I. There were no significant differences in any of the test results when compared to results from non-radiated control samples.

Example 4: Foamed PET Tray

Mono-layered polyester foamed trays were prepared as described in Example 3. The trays were subjected to an electron beam radiation source with a dosage of 7.0 kGy. Testing was done as described in Example 1. The results are found in Table I. There were no significant differences in any of the test results when compared to results from non-radiated control samples.

Example 5: Non-Foamed PET Tray (Comparative Example)

Rigid, non-foamed polyester sheeting material was formed into trays. The trays were about 6 inches (150 mm) x 8 inches (200 mm). The sheet was about 0.020 inch (0.50 mm) thick prior to forming of the trays. The trays were subjected to a gamma radiation source with a radiation dosage of 7.6 kGy to simulate a radiation sterilization process. The trays were tested as in Example 1 and compared to non-radiated control samples. The results are found in Table I.

Example 6: Non-Foamed PET Tray (Comparative Example)

Rigid, non-foamed polyester trays as described in Example 5 were subjected to an electron beam radiation source with 7.0 kGy dosage. The trays were tested as in Example 1 and compared to non-radiated control samples. The results are found in Table I.

Table I

Data Before and After Irradiation for PET Samples

Example No.		1	2	3	4	5	6
Analysis		Med Density FoamedTray	MedDensity FoamedTray	LowDensity FoamedTray	LowDensity FoamedTray	Comparative Example Solid Tray	Comparative Example Solid Tray
Irradiation Dosage		7.6 kGy	7 kGy	7.6 kGy	7 kGy	7.6 kGy	7 kGy
Irradiation Source		Gamma	e-Beam	Gamma	e-Beam	Gamma	e-Beam
IV:Before Treatment dl/g		0.69	0.69	0.89	0.89	0.70	0.70
IV: After Treatment dl/g		0.69	0.69	0.88	0.88	0.70	0.70
DSC - Second Cycle							
Before:	Tg °C	80	80	80	80	81	81
	Tch °C	136	136	134	134	136	136
	Tm °C	247	247	246	246	249	249
	Tcc °C	194	194	191	191	175	175
	% Cryst	26.1	26.1	38.3	38.3	22.3	22.3
After:	Tg °C	80	80	81	81	82	81
	Tch °C	135	136	135	134	136	136
	Tm °C	247	247	246	246	249	249
	Tcc °C	196	195	191	191	174	175
	% Cryst	29.3	27.6	38.5	34.3	21.3	23.5

GPC: Before							
	Mn	15610	15610	17142	17142	17168	17168
	Mw	52234	52234	84481	84481	51950	51950
	Mz	97809	97809	210584	210584	83817	83817
	Pdispersity	3.346	3.346	4.928	4.928	2.973	2.973
GPC: After							
	Mn	15683	15948	17128	18005	16815	16838
	Mw	53385	54001	85208	83104	51829	51858
	Mz	102937	104430	215160	204338	85984	86541
	Pdispersity	3.404	3.386	4.975	4.616	3.082	3.08
Color (ASTM D2244)							
Before:	L*	88.5 (0.18)	88.5 (0.18)	91 (0.07)	91 (0.07)	91 (0.15)	91 (0.15)
	a*	-1.31 (0.02)	-1.31 (0.02)	-0.71 (.006)	-0.71 (.006)	-1.90 (0.035)	-1.90 (0.035)
	b*	1.56 (0.22)	1.56 (0.22)	-0.08 (0.01)	-0.08 (0.01)	1.07 (0.16)	1.07 (0.16)
After:	L*	88.5	89.4 (0.7)	91.5 (0.05)	91.6 (0.08)	91.5 (0.5)	91.6 (0.7)
	a*	-1.23 (0.03)	-1.22 (0.05)	-0.65 (.006)	-0.61 (0.03)	-1.86 (0.1)	-1.89 (0.11)
	b*	1.08 (0.12)	1.74 (0.04)	-0.29 (0.04)	-0.39 (0.04)	1.64 (0.5)	1.66 (0.7)
ASTM D882 Tensile Before							
Tensile @ Yield, Mpa	No direction	16.9 (0.5)	16.9 (0.5)	No Yield	No Yield	57.7 (3.2)	57.7 (3.2)
Tensile @ Break, Mpa	No direction	15.9 (1.8)	15.9 (1.8)	7.7 (0.4)	7.7 (0.4)	46.3 (17.3)	46.3 (17.3)
Elongation @ Break, %	No direction	3.9 (1.1)	3.9 (1.1)	87.8 (17.5)	87.8 (17.5)	5.2 (1.2)	5.2 (1.2)
Secant Modulus, Mpa	No direction	670 (22)	670 (22)	228 (11)	228 (11)	1793 (78)	1793 (78)

ASTM D882 Tensile After							
Tensile @ Yield, Mpa	No direction	17.2 (0.9)	17.3 (1.1)	No Yield	7.1 (0.3)	58.1 (3.1)	54.3 (4.9)
Tensile @ Break, Mpa	No direction	16.7 (0.9)	17 (0.8)	6.2 (0.6)	7.3 (0.2)	47.1 (6.6)	35.9 (6.2)
Elongation @ Break, %	No direction	3.5 (0.7)	3.3 (0.3)	87.1 (14.2)	62 (21)	88.8 (134)	151 (181)
Secant Modulus, Mpa	No direction	723 (31)	729 (47)	184 (15)	215 (20)	1767 (68)	1728 (79)
Notes	Numbers in parentheses represent standard deviation of data. Before data is from non-radiated control samples. After data is from radiated samples after radiation.						

CLAIMS

We claim:

1. A package containing an article sterilized by irradiation comprising:
   a) an article enclosed in a space defined by surrounding packaging comprising a foamed polyester, and
   b) a sterilized environment formed by irradiating the space.
2. The package according to claim 1, wherein the article comprises a food product.
3. The package according to claim 1, wherein the article comprises one or more medical instruments.
4. The package according to claim 1, wherein the packaging comprises a tray and a lid.
5. The package according to claim 4, wherein the tray consists substantially of the foamed polyester.
6. The package according to claim 4, wherein the tray and the lid consist substantially of the foamed polyester.
7. The package according to claim 1, wherein the polyester has repeat units from a diacid component comprising at least 65 mole percent of the diacids selected from the group consisting of terephthalic acid, naphthalenedicarboxylic acid, 1,3-cyclohexanedicarboxylic acid, 1,4-cyclohexanedicarboxylic acid, and mixtures thereof, based on a diacid component of 100 mole percent.
8. The package according to claim 1, wherein the polyester has repeat units from a glycol component comprising at least 65 mole percent of the glycols selected from the group consisting of ethylene glycol, neopentyl glycol, 1,3-cyclohexanemethanol, 1,4-cyclohexanemethanol, and mixtures thereof, based on a glycol component of 100 mole percent.

9. The package according to claim 1, wherein the irradiation has a source selected from the group consisting of electron beam sources and radioactive sources.

10. The package according to claim 1, wherein the irradiation has a cobalt 60 radioactive source.

11. The package according to claim 1, wherein the amount of irradiation is about 1 kilogray to about 10 kilograys.

12. The package according to claim 1, wherein the foamed polyester has a crystallinity of about 2 percent to about 40 percent.

13. The package according to claim 1, wherein the foamed polyester has a density of about 0.1 grams/cubic centimeter to about 1.0 grams/cubic centimeter.

14. The package according to claim 4, wherein the tray comprises a mono-layer structure.

15. The package according to claim 4, wherein the lid comprises a mono-layer structure.

16. The package according to claim 4, wherein the lid comprises an essentially clear film.

17. A method comprising the step of sterilizing, by irradiation, an article packaged within packaging comprising foamed polyester.

18. The method according to claim 17, wherein the article comprises a food product.

19. The method according to claim 17, wherein the article comprises one or more medical instruments.

20. The method according to claim 17, wherein the packaging comprises a tray and a lid.

21. The method according to claim 20, wherein the tray consists substantially of the foamed polyester.

22. The method according to claim 20, wherein the tray and the lid both consist substantially of the foamed polyester.

23. A method for making a sterilized packaged article comprising the step of irradiating the article within packaging comprising foamed polyester.

24. The method according to claim 23, wherein the article comprises a food product.

25. The method according to claim 23, wherein the article comprises one or more medical instruments.

26. The method according to claim 23, wherein the packaging comprises a tray and a lid.

27. The method according to claim 26, wherein the tray consists substantially of the foamed polyester.

28. The method according to claim 26, wherein the tray and the lid both consist substantially of the foamed polyester.

29. The sterilized packaged article made by the method of claim 23.

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(54) Title: FOAMED POLYESTERS FOR IRRADIATED STERILIZATION PACKAGING

(57) Abstract: The invention provides packages comprising articles sterilized by irradiation and packaged within foamed polyester packaging. The invention also provides methods for the sterilization, by irradiation, of articles contained within foamed polyester packaging. The sterilized articles include food products, medical instruments, and other articles which are typically sterilized before consumption or use. The packaging may comprise a mono-layer or multi-layer structure. The irradiation can be created by various radiation sources such as an electron beam source or a radioactive source. The foamed polyester is made from repeat units of a diacid component having at least 65 mole percent terephthalic acid, naphthalenedicarboxylic acid, 1,3-cyclohexanedicarboxylic acid, 1,4-cyclohexanedicarboxylic acid, or mixtures thereof, and repeat units of a glycol component having at least 65 mole percent ethylene glycol, neopentyl glycol, 1,3-cyclohexanemethanol, 1,4-cyclohexanemethanol, or mixtures thereof.

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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 602 965 A (ETHICON) 22 June 1994 (1994-06-22) column 4, line 15 - line 22 column 4, line 38 - line 55; figures ---	1,3-5,9, 17, 19-21, 23, 25-27,29
X	US 5 176 258 A (ANTAL) 5 January 1993 (1993-01-05) column 5, line 38 - line 44 column 7, line 11 - line 18; figures --- -/--	1,3-5,9, 17, 19-21, 23, 25-27,29

[X] Further documents are listed in the continuation of box C.

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International Application No
PCT/US 01/24977

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 392 910 A (BELL ET AL.) 28 February 1995 (1995-02-28) column 3, line 24 - line 36 column 3, line 52 - line 55; figures ---	1,3-5,9, 17, 19-21, 23, 25-27,29
A	US 4 324 331 A (IGNASIAK) 13 April 1982 (1982-04-13) column 2, line 43 - line 59 column 4, line 7 - line 14; figures ---	1,3-5,9, 14-17, 19-23, 25-29
A	US 4 652 763 A (NABLO) 24 March 1987 (1987-03-24) the whole document ---	1,2,4-6, 9,10, 14-18, 20-24, 26-29
A	EP 0 261 929 A (KEYES) 30 March 1988 (1988-03-30) the whole document -----	1,2,4-6, 9,10, 14-18, 20-24, 26-29

1

IN :RNATIONAL SEARCH REPORT

Information on patent family members

Inte, ,tional Application No
PCT/US 01/24977

Patent document cited in search report		Publication date	Patent family member(s)			Publication date
EP 602965	A	22-06-1994	US	5356006	A	18-10-1994
			AU	673861	B2	28-11-1996
			AU	5246693	A	30-06-1994
			CA	2111365	A1	17-06-1994
			DE	69319704	D1	20-08-1998
			DE	69319704	T2	11-03-1999
			EP	0602965	A2	22-06-1994
			JP	6255682	A	13-09-1994
			US	5325987	A	05-07-1994
US 5176258	A	05-01-1993	CA	2062011	A1	04-10-1992
US 5392910	A	28-02-1995	NONE			
US 4324331	A	13-04-1982	NONE			
US 4652763	A	24-03-1987	CA	1246316	A1	13-12-1988
			CN	85109042	A	08-10-1986
			DE	3585389	D1	26-03-1992
			EP	0197217	A2	15-10-1986
			JP	2096349	C	02-10-1996
			JP	8004613	B	24-01-1996
			JP	61226050	A	07-10-1986
EP 261929	A	30-03-1988	AU	7893687	A	31-03-1988
			BR	8704862	A	17-05-1988
			CN	87107584	A	20-04-1988
			DK	496987	A	24-03-1988
			EP	0261929	A2	30-03-1988
			JP	63203527	A	23-08-1988
			NO	873952	A	24-03-1988
			ZA	8707120	A	31-08-1988